EFFECT OF VELOCITY IN EROSION CORROSION

MOHD KHAIRUL NA'IM BIN MOHD ARIFFIN

Thesis submitted in partial fulfillment of requirements for the award of Bachelor of Mechanical Engineering

Faculty Of Mechanical Engineering

UNIVERSITI MALAYSIA PAHANG

JUNE 2012

ABSTRACT

The present study has been conducted to investigate the interaction effect of velocity on erosion corrosion of material in aqueous slurries. Tests were performed on stainless steel samples of grade 301. Pure erosion and pure corrosion as well as erosion corrosion impingement tests were carried out at two different impact velocities 500 rpm, 1000 rpm and also without any velocity. The erosion corrosion test was carried out by immersing the specimen in an aqueous 3.5% NaCl solution and presence of sand particles. Electrochemical Erosion Corrosion Test have been conducted and reported in this thesis. The data then analyze using Ivman software to determine the value of corrosion rate. The surface image and surface roughness value was taken before and after the Electrochemical Erosion-Corrosion test. From observation of the result, when the value of velocity increases the corrosion rate also increases. Besides that, the value of surface roughness also increase when the corrosion rate increase due to present of pitting corrosion.

ABSTRAK

Kajian ini telah dijalankan untuk mengkaji kesan interaksi halaju pada kakisan hakisan bahan di dalam larutan akueus. Ujian telah dijalankan ke atas sampel keluli tahan karat gred 301. Pengaratan hakisan dan kakisan telah dijalankan di dua kesan halaju yang berbeza 500 rpm, 1000 rpm dan juga tanpa halaju. Ujian hakisan kakisan telah dijalankan dengan merendamkan spesimen di dalam larutan akueus 3.5% NaCl dan kehadiran pasir. Ujian elektrokimia kakisan hakisan telah dijalankan dan dilaporkan di dalam tesis ini. Data diperolehi daripada ujian elektrokimia dianalisis menggunakan perisian Ivman untuk menentukan nilai kadar kakisan. Imej permukaan dan nilai kekasaran permukaan telah diambil sebelum dan selepas ujian elektrokimia kakisan hakisan. Daripada pemerhatian keputusan, apabila nilai halaju meningkatkan kadar kakisan juga meningkat. Selain itu, nilai kekasaran permukaan juga meningkat apabila kadar kakisan meningkat disebabkan kehadiran kakisan berbintik.

TABLE OF CONTENT

LIST OF TABLE

LIST OF FIGURE

LIST OF ABBREVIATION

Nacl	Sodium Chloride
Rpm	Rotational Per Minute
Fe	Ferrous
℃	Celsius
e^-	Electron
H_2O	Water
O_2	Oxygen
OH^-	Oxide
Cl^-	Chlorine
FeCl	Ferrous Chloride
SCE	Saturated Colonel Electrode
E	Potential
V	Volt
A/ cm^2	Current Density

CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

Erosion-corrosion actually arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion. Virtually all metal alloys, to one degree or another, are susceptible to erosion corrosion. It is especially harmful to alloys that passivity by forming a protective surface film the abrasive action may erode away the film, leaving exposed a bare metal surface. Relatively soft metals such as copper and lead are also sensitive to this form of attack. Usually it can be identified by surface grooves and waves having contours that are characteristic of the flow of the fluid. Increasing fluid velocity normally enhances the rate of corrosion. Also, a solution is more erosive when bubbles and suspended particulate solids are present.

Erosion–corrosion is commonly found in piping, especially at bends, elbows, and abrupt changes in pipe diameter positions where the fluid changes direction or flow suddenly becomes turbulent. Propellers, turbine blades, valves, and pumps are also susceptible to this form of corrosion. In offshore well systems, the process industry in which components come into contact with sand-bearing liquids, this is an important problem. Materials selection plays an important role in minimizing erosion corrosion damage. Caution is in order when predicting erosion corrosion behavior on the basis of hardness. High hardness in a material does not necessarily guarantee a high degree of resistance to erosion corrosion. Design features are also particularly important.

Erosion-corrosion tests were carried out by immersing the materials in an aqueous solution and presence of sand particles. Combine erosion corrosion effect were

studied by partially protecting the materials from the impact of solid particles during the test. Erosion corrosion mechanisms were determined from micro structural studies by light microscopy.

1.2 PROBLEM STATEMENTS

It is well known that the industries that transport slurries and other particle-laden liquids in pipes for sectors such as offshore and marine technologies spend millions of pounds every year to repair material damage. The typical examples of this kind of material destruction are erosion–corrosion damage to pumps, impellers, propellers, valves, heat exchanger tubes and other fluid handling equipment. In a recent survey, erosion–corrosion was rated in the top five most prevalent forms of corrosion damage in the oil and gas industry (P. McIntyre, 1999). When corrosion and erosion act together the damage mechanism are complex and generally the measured mass loses are higher than the sum of separate material losses due to corrosion and erosion.

So, the erosion corrosion test was carried out by immersing the specimen in an aqueous 3.5% NaCl solution and presence of sand particles. First, the value of roughness is determines. The surface micro structural also was study before start the experiment. It was done without any velocity and by two different rate of velocity which 500 rpm and 1000 rpm where the impact angle of the slurry against the surface is 90° and at the ambient temperature.

1.3 PROJECT OBJECTIVE

To study the surface roughness and corrosion rate of material (stainless steel) in aqueous slurries with different rate of velocity.

1.4 SCOPE

The focus area will be done on the following aspect:

(i) Different rate of velocity where 0, 500 and 1000 rpm.

(ii) The specimen immersing in an aqueous 3.5% NaCl solution and 10 wt% presence of sand particles.

(iii) The impact angle of the slurry against the surface is 90°.

(iv) At ambient temperature 27°C- 30°C.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The discussion is limited to the potential effect of fluid velocity on metal loss and the consequence on the erosion velocity. The localized corrosion rate is a function of multiple variable, which include fluid chemistry, tube metallurgy, and accelerating factor of flow rate and sand production. The effect of corrosion on solid particle erosion is to provide a brittle target for the solid particle. The combination process of erosion corrosion has a number of potential effects depending on the relative rates of each of the individual process. If the mechanical action of erosion removes or reduces the thickness of this scale, then the stifling process is reduced or does not occur. This combined process in term erosion-corrosion. It is clear that the rate of the scale growth and the rate of scale thinning govern the total metal loss. When the rate of scale growth is significantly greater than scale thinning, the scale thickness will increase, the rate of metal loses decrease and the total metal loss is due to corrosive action. When the rate of scale thinning is significant greater than the scale growth, the effect is metal loss due to pure erosion. However, the composition of the metal surface have been altered due to corrosive action and if the surface hardness is decrease due to depletion of the alloying element, then the erosion rate is greater than that which would be expected due to pure erosion. The prediction of corrosive damage is an extremely complex issue that does play a role in the erosion-corrosion process. The scale composition, scale mechanical properties, and resulting damage are specific to the chemistry of the following fluid and the metallurgy of the pipe wall. However, for the case with sand present the functional relationship for erosion velocity and sand production is similar to pure erosion even though the magnitude may be greater when corrosion is present. The rate of metal loss is increased with an increase in velocity, but the process is somewhere different.

$$W = \frac{\theta(c_{e-}c_{\infty})}{\left(\frac{1}{k}\right)+(1-f)[\left(\frac{1}{h_4}\right)+\left(\frac{d}{D}\right)]} \quad (2.1)$$

Where:

W = wear rate

C_e = equilibrium concentration of iron species

θ = porosity of open area of metal

h_4= mass transfer coefficient

k = A exp, the reaction rate constant

f = fraction of oxidized metal into magnetic at the metal- oxide interface

D = Diffusion coefficient

d = oxide thickness

C_∞= iron species concentration in the bulk of the fluid

The effect of velocity was to increase the mass transfer coefficient. The conclusion is the flow of condensate increase the rate of arrival of the corrosive species to the metal surface and the rate of removal of the corrosion product from the surface and, therefore increases the rate of corrosion. (Danny M.Deffenbaugh,J.Christopher Buckingham,1989)

2.2 The Mechanisms of Erosion: Brittle versus Ductile

Brittle erosion involves the impact of particles on the surface of the metal which cause cracks to propagate down through the metal surface. These cracks propagate throughout the metal and lead to chunks of metal being chipped away by repeated impact of particles. This type of erosion occurs because the metal has little tendency to strain which causes it to fracture.

As opposed to brittle erosion, ductile erosion involves the impact of particles which plastically deform the surface of the metal. The repeated impact of particles forges hardened platelets on the surface of the metal and this creates a transient response in the erosion process and this process is termed the platelet formation theory of erosion. Work hardening of the metal subsurface occurs for ductile metals undergoing

erosion due to the extensive plastic deformation at the metals surface. This leads to a transient response in the erosion process for a ductile metal at which time the surface of the metal is being work hardened and platelets are being formed. The steady-state response occurs after the platelets are formed.

The process of erosion for a ductile metal, such as carbon steel, occurs by the followings steps. First a single particle is impinged upon the surface of the target metal. This initial impingement creates a crater in the metal surface which removes little to no material. Subsequent impacts on the metal surface forge platelets from the deformations caused by the extrusion process. During this time there is also work-hardening of the metal subsurface occurring.

The impact of the particle on the surface of the metal carries a much greater force than that required to form platelets. This energy is transferred into the subsurface of the metal where the metal is cold worked, creating a less ductile subsurface below the platelet surface. The result of platelet formation is a harder surface which now allows particles to impinge and chip away at the platelets. The mechanism of erosion is dependent on the type of material that is being eroded. Harder metals will tend to erode by brittle erosion mechanisms and softer metals will erode by ductile erosion mechanisms. It should be noted that it is possible to have a metal where both mechanisms are occurring simultaneously. One example of this would be in alloyed metals with very coarse grain structure. It could be that one of the components of the alloy erodes in a ductile manner and one in a brittle manner. (Levy Av, 1995)

2.2.1 Particle Impact and Velocity

It would be expected that as the velocity of the particle increases the greater the erosion damage upon impact and much experimental evidence from researchers such as Levy.(Levy Av, 1995), (Nesic and Postlethwaite, 1993), (Salama, 2004) have shown this.

$$\text{Kinetic energy} = \tfrac{1}{2} MV^2 \qquad (2.2)$$

Where:

M = mass
V = velocity

The faster a particle moves the more kinetic energy it has based on the equation for kinetic energy equation 2.2. Therefore, it would be expected that as the velocity increases the erosion rate would increase and most likely in non-linear manner. If the erosion rate is proportional to the kinetic energy of the particle then it would be likely that erosion rate is proportional to the square of the velocity. However, only part of the velocity component is lost upon impact on the metal surface because the particle is under constant movement due to flow and therefore not all of the particles energy is transferred to the metal surface (Levy ,1995).It should be noted that increasing the velocity increases the erosion rate for both brittle and ductile metals although they erode by different mechanisms.

Surface analysis for 1018 carbon steel shows that erosion tests using an impingement jet with velocities ranging from 15-130 m/s show that the mechanism of platelet formation occurs over this entire range of velocities. This suggests that the mechanism of erosion does not change with increasing velocity for a ductile metal (Levy, 1995). The corrosion rate on the surface is enhanced as the bare metal is exposed following erosion or the coating adhesion is affected. At higher velocity the crater volume will increase due to the higher particle kinetic energies. The literature also suggests that with increasing velocities the corrosion currents will increase due to the higher mass transfer at such velocities and hence will also enhance the formation of passive films by the transport of oxygen to the reaction site. The frequency of the particles impacting the surface will increase as the velocities increases causing a change in the rate of depassivation and repassivation leading corrosion currents to increase

2.2.2 Particle Size

The reason for this is because as the particle increases in size the surface area of the particle increases as well (Levy, 1995). This means there is more particle surface which will contact the metal surface upon impact which will lead to the force upon

impact being spread out over a wider area (Levy, 1995). This will lead to a shallower depth of penetration and therefore the erosion damage will not significantly change even though the mass and size of the particle is greater. Another reason for this phenomenon is that as particles increase in size there are more particle interactions which may inhibit certain particles from contacting the metal surface. Larger particles at the metal surface may hinder other particles from coming in contact with the surface. Particles less than 175 micron yielded lower erosion rates than those in the range of 175-900 microns given above (Nesis.S and J.postlethwaite, 1993). This is because the smaller particles have less kinetic energy and therefore cause less erosion damage (Levy, 1995).

2.2.3 Particle Shape

Sharper particles tend to have higher erosion rates associated with them than duller, more spherical shaped particles. This is because sharper particles can penetrate deeper into the metal surface (Levy, 1995) (Nesis.S and J.postlethwaite, 1993).Sharper particles also have a smaller contact area at the metal surface so the force generated is much larger. A spherical shaped particle has little penetration power and the exposed area is greater which means there is the same amount of force exerted as a sharper particle but over a larger area of the metal surface. Although smooth, spherical particles do erode metals, the erosion rates are significantly less than sharper particles such as sand (Nesis.S and J.postlethwaite, 1993).

2.2.4 Metal Loss Rate

The simplest method for measuring the erosion rate of a material is by measuring the weight loss of a metal sample before and after being subjected to an erosive condition (Levy A.V, 1995).In this study the erosion rates will be calculated using the following equation 2.2 .(Jones, Denny A 1996)

$$\text{Metal Loss Rate} = \frac{W}{\rho / A.T} \qquad (2.3)$$

Where W is the weight loss, ρ is the density of the metal, A is the exposed area, and T is time. This calculation can be used for corrosion and erosion weight loss data to determine the metal loss rate.

2.3 Erosion corrosion mechanism

Corrosion of metals takes place through the action of electrochemical cells. Although this single mechanism is responsible, the corrosion can take many forms. Through an understanding of the electrochemical cell and how it can act to cause the various forms of corrosion, the natural tendency of metals to corrode can be overcome and equipment that is resistant to failure by corrosion can be designed.

The corrosion resistance of stainless steel is achieving through the formation of a thin chromium oxide film layer on the surface of the material (Callister WD, 2007). However, when this material is exposed to erosion-corrosion condition, the mechanical damage of the passive film from the solid particle suspended in the corrosive fluid can lead to passive film breakdown. (Renould L.Abrasion et al., 1998)

2.3.1 Basics of Fe^{2+} Corrosion

a) Pitting Initiation

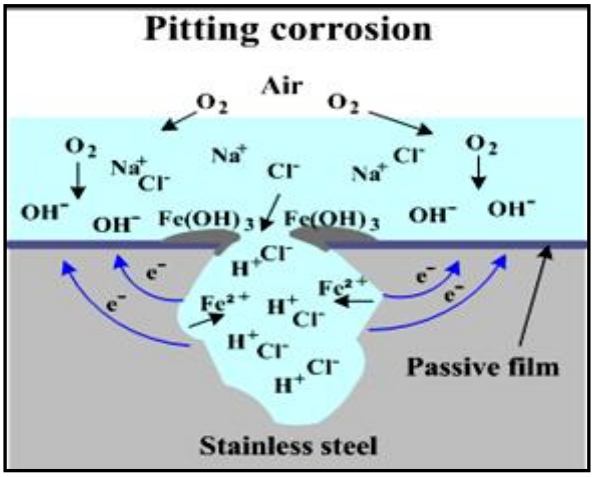

Figure 2.1: Pitting Corrosion

(Source: Dr. Dmitri Kopeliovich,2008)

At the initial pit a form on the surface as passive oxide film. Affect from the scratches it make a mechanical damage on the passive film then the anodic reaction will expose to the electrolyte. The passivated surrounding will act as the cathode. Particles on a second phase was emerge on the metal surface the particle receipting along the grains boundaries may function as local anodes causing formation of initial pits.

b) Pitting Growth

Present the chloride ions will initial the pitting growing. The anodic reaction inside the pit:

$$Fe = Fe^{2+} + 2e^{-} \text{ (dissolution of iron)} \quad (2.4)$$

The electron the will given up by the anode flow to the cathode (passivated surface) whee they are discharge in the cathodic reaction:

$$1/2O_2 + H_2O + 2e^{-} = 2(OH^{-}) \quad (2.5)$$

As a result, this reaction will on the electrolyte enclosed in the pit gain positive electrical charge in contrast to the electrolyte surrounding the pit, which become negatively charged. Then the positive charged pit attract negative ion of chlorine Cl- to increasing acidity of the electrolyte according to the reaction.

$$FeCl_2 + 2H_2O = Fe(OH)_2 + 2HCl \quad (2.6)$$

From the equation PH value of the electrolyte inside the pit decrease from 2 until 3 which causes a further acceleration in the corrosion process. Then the corrosion rate will increase cause of the large ratio between the anode and cathode. Corrosion products ($Fe(OH)_3$) form around the pit resulting in further separation of its electrolyte.

2.3.2 Measuring Corrosion Rate

The corrosion process can be monitored in order to determine the actual rate of metal loss occurring on the target metal. Electrochemical measurements can be made in order to determine the actual current flowing through the target metal. This current is

called the corrosion current and is directly proportional to the corrosion rate. As the potential between the corroding metal and the cathode gets larger, the corrosion current increases up to a point where the current no longer changes with increasing potential difference. This point is called the limiting current and is limited due to the transfer of charges from the metal to the cathode. When the limiting current is reached there are more electrons at the metal surface than the cathodic specie can consume.(Jones and Denny, 1996)

The corrosion rate can be obtained through the use of a potentiostat. A potentiostat controls the voltage difference between a working electrode and a reference electrode. The working electrode is the metal which is being tested and the potentiostat controls the potential of the metal and measures the current passing through the working electrode. The reference electrode is used to measure the potential of the working electrode. Since potential is relative there needs to be a stable reference electrode that maintains the same potential throughout the experiment. The electrons flow from the working electrode to the counter or auxiliary electrode which completes the circuit. (Jones and Denny, 1996)

In order to test the corrosion rate of a metal, the corrosion potential of the target metal is tested first. The corrosion potential is the potential of the non-polarized target metal in the corrosive solution. A potentiodynamic sweep polarizes the target metal at a given voltage above and below the corrosion potential. The current is monitored at each incremental change in the potential difference. At potentials lower than the corrosion potential (more negative) the sweep shows the current versus potential curve for the cathodic reactions and at potentials higher than the corrosion potential (more positive) the sweep shows the current versus potential curve for the anodic reaction. The corrosion current can be measured directly from the plot of the potentiodynamic sweep by extending the linear portions of the anodic and cathodic curves until they cross at the corrosion potential. The current at which these two lines intersect is the corrosion current.

When the potential of an electrode is plotted as a function of the logarithm of currentdensity, then this is called a Tafel plot(Jones and Denny, 1996). The straight line

portions of the curves which can be extrapolated to determine the corrosion current are called the Tafel lines(Nesic et al.,2003). The slopeof the Tafel lines is defined as the Tafel slope. The equation for each Tafel line is given as :

$$\eta = \frac{2.3\ RT}{\alpha nF}\log_0 i \ - \ \frac{2.3\ RT}{\alpha nF}\log i \qquad (2.7)$$

Where η is the over potential, R is the ideal gas law constant, T is temperature, α is the cathodic electron transfer coefficient, n is the number of equivalents exchanged, and F is Faraday's constant (96,500 coulombs/equivalent), io is the exchange current density, and I is the current at the given over potential.(Jones and Denny,1996).

As the over potential is shifted more negatively then the cathodic reaction or reactions will be accelerated and the anodic reaction will be decreased (Jones and Denny ,1996). The difference between the increase in the cathodic reduction rate and the decrease in the anodic oxidation rate is equal to the applied current:

$$i_{app,c} = \ i_c - \ i_a \qquad (2.8)$$

As the cathodic over potential increases there is a point where the anodic current density becomes insignificant when compared to ic and therefore the straight line portions of the Tafel plot are seen. This linear behavior at high cathodic over potentials is referred to as Tafel behavior.

Using the polarization resistance method the corrosion current can be directly measured from polarization data. For small deviations in the over potential (up to 20 mV from the corrosion potential) the plot of over potential versus applied current is linear. The slope of this line is the polarization resistance for the electrode.(Jones, Denny A,1996).

$$R_p = \frac{\Delta \mathrm{E}}{\Delta \mathrm{i_{app}}} \qquad (2.9)$$

The corrosion current can be measured directly from the polarization resistance usingthe proportionality constant. The proportionality constant is calculated from the anodic and cathodic Tafel slopes, βa and βc, from the following equation.(Jones, Denny A,1996):

$$B = \frac{\beta_a \beta_c}{2.3\,(\beta_a + \beta_c)} \tag{2.10}$$

The corrosion current can then be calculated from the proportionality constant and the polarization resistance from the equation :

$$i_{corr} = \frac{B}{R_p} \tag{2.11}$$

2.3.3 Correlation Between Current Flow and Weight Loss

For each specific anodic reaction a characteristic number of electrons are produced in the reaction of one metal ions. Thus, all other things being equal, the metal loss is proportional to the number of electrons that are produced. As the electrons produced migrate to cathodic areas through the electron path, the metal loss is proportional to the current flow. In cases where more positively charged ions are produced, more electrons flow for a given number of corroding metal atoms but the current flow remains proportional to the metal loss. (NAVFAC, 1992)

2.4 Electrochemical Impedance Spectroscopy (EIS)

In an electrochemical cell there is a solution resistance that creates a voltage drop along the path of the current. Therefore, the potential measured between the reference and working electrode has an error associated with it due to the resistance of the solution. This solution resistance is increased as the reference electrode is moved farther from the working electrode. In corrosion measurement techniques there is always going to be some distance between the reference and working electrode and thus solution resistance will cause an inaccuracy in the corrosion rate measurement. All electrochemical cells have a solution resistance; however, for some testing this solution

resistance may be insignificant when compared to the overall polarization resistance of the working electrode. If the solution resistance is significant then it is subtracted from the polarization resistance measured on the working electrode.

To correct for solution resistance the reference and working electrode can be considered a capacitor with the solution between them acting as the dielectric. When a direct current is passed through an electrochemical cell the resistance through the system is a sum of the solution resistance (capacitance) and the polarization resistance of the working electrode. High frequency alternating currents passed through the electrochemical cell will directly measure the solution resistance of the electrochemical cell by measuring the resistance of the equivalent ohmic resistive element. At very low alternating current frequencies the current is more like a direct current and the resistance measured is once again the sum of the ohmic solution resistance and the polarization resistance. Using a large range of frequencies, the polarization resistance of the working electrode can be determined by taking the difference between the low end alternating frequency currents and the high frequency currents. This procedure for measuring solution resistance is called electrochemical impedance spectroscopy (EIS).(Jones and Denny,1996):

2.5 Microbiological effects on corrosion in seawater

Seawater is an excellent electrolyte. The presences of a large amount of dissolved salts, sodium chloride (NaCl), that are ionized make it an excellent conductor. The chloride ions are particularly aggressive as it causes a breakdown of passivity. The chloride ion is also particularly aggressive as most chloride compounds are highly soluble, which limits the formation of polarizing anodic films. Seawater also usually contains enough dissolved oxygen for reducing water to be theprevalent cathodic reaction in most cases.(NAVFAC, 1992)

The exposure of any material to natural seawater initiates a series of sequential and parallel biological and chemical events that culminate in the formation of a complex layer of inorganic, organic, and cellular components known as biofouling. The accumulation of bacteria, fungi, and microalgae and their secretions is collectively